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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE DETERMINATION OF SMALL AMOUNTS OF ANTIMONY BY THE BERZELIUS-MARSH PROCESS.

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WITH A PLATE.

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The Berzelius-Marsh method has been successfully applied to the quantitative determination of arsenic. On the one hand, the process which depends upon the weighing of the "mirror," first suggested by Berzelius himself,[1] has been carefully worked out by Gautier,[2] Chittenden and Donaldson,[3] and several others, and is applicable to cases in which the amount of arsenic is too small for precipitation as sulphide or in which the separation of the latter would be inconvenient. On the other hand, for cases in which the mirror of arsenic is too small for weighing, or in the rapid estimation of very small amounts, methods similar to that which was first described by one of us[4] have found wide application.

The extension of the gravimetric Berzelius-Marsh method to the determination of antimony is impossible for the reason that, under ordinary circumstances, a large part of the antimony is deposited on the zinc in the reduction flask and does not leave the solution as the hydride. In attempting to apply the method of Sanger[4] to the determination of small amounts of antimony, we were met not only by this difficulty, but also by the well-known irregularity in the deposition of the antimony in the heated tube, the temperature at which the antimony hydride is decomposed being so low that much of the deposit is formed

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[1] Berzelius, Jahresbericht, **17**, 191 (1837). The decomposition of the arsenic hydride by heating the tube was also suggested by Liebig, Ann., **23**, 217 (1837), but the idea of weighing the arsenic seems to have originated with Berzelius.

[2] Bull. Soc. Chim. (2) **24**, 250 (1876).

[3] Am. Chem. Journ., **2**, 235 (1881); Chem. News., **43**, 21 (1881).

[4] These Proceedings, **26**, 24 (1891); Amer. Chem. Journ., **13**, 431 (1891). Abstracted in Jour. Chem. Soc., **62**, 382 (1892); Jour. Soc. Chem. Ind., **11**, 370 (1892); Chem. Centralbl., **63**, 335 (1892); Ber., **25**, 47, r, (1892); Zeitschr. Anal. Chem., **38**, 137 and 377 (1899).

in the wide part of the tube; hence a series of standard mirrors under these conditions is impossible. We have found, however, that both of these obstacles are surmountable, and that small amounts of antimony in solution can be reduced with practical completeness to the hydride, which, when suitably heated, deposits the antimony in such a form as to admit of estimation with reasonable accuracy by comparison with standard mirrors.

In arriving at this result two studies were made: first, as to the influence of the concentration of the antimony ions on the deposition of the antimony upon the zinc; second, as to the influence of the temperature and cross section of the heated tube on the formation of the mirror.

I. The Evolution of Antimony Hydride in the Reduction Flask.

A solution of pure recrystallized tartar emetic was prepared of such a strength that 10 grams contained 0.0996 gram of metallic antimony (average of five determinations of the antimony as the pentasulphide, also confirmed by the volumetric method given below). A definite amount of this solution was introduced in small portions into the reduction flask (see Figure 2), which contained 0.5 gram of zinc and 20 cubic centimeters of dilute sulphuric acid (1 to 12). The evolved hydride was carried through a hot tube by a current of hydrogen according to the method described below, except that the tube was heated, as in the determination of arsenic, at its wide portion. After the deposition of the antimony in the heated tube had evidently reached its maximum, we determined the amount of the deposit, as well as the amount precipitated on the zinc and the residue still in solution. The volume of liquid in the reduction flask was approximately the same in all cases.

To find the amount of antimony deposited in the heated tube, the portion of the tube containing the deposit was weighed, the mirror dissolved in hydrochloric acid and potassic chlorate, and the tube, after washing with alcohol and ether, reweighed.

The metallic antimony and zinc left in the reduction flask were filtered, washed, and dissolved in hydrochloric acid with the aid of a small amount of potassic chlorate. The antimony in this solution was determined by the iodometric method of Gooch and Gruener.[5] The solution, free from chlorine, was reduced by boiling with potassic iodide in excess of sulphuric and tartaric acids. Any residual iodine was bleached by careful addition of approximately hundredth-normal sul-

[5] Amer. Journ. Sci., **42**, 213 (1891).

phurous acid, and the solution, neutralized with sodic hydroxide, was titrated with iodine after addition of acid sodic carbonate.

In the filtrate from the metallic antimony and zinc, the unreduced antimony in solution was determined also by titration with iodine.

Four series of determinations were made, using weighed amounts of the tartar emetic solution equivalent respectively to about 150, 100, 50, and 10 milligrams of antimony. The results are given in the following table. The analyses under columns *c* and *d* were made, in Series A and B, with an approximately decinormal solution of iodine, standardized, through sodic thiosulphate and potassic bichromate, against pure iron. In Series C and D an approximately centinormal solution of iodine was used, standardized against a determinate solution of thiosulphate made from the decinormal.

TABLE I.

No.	*a* mg. Sb. taken.	*b* mg. Sb. dep. in tube.	*c* mg. Sb. ppted on zinc.	*d* mg. Sb. not reduced.	*e* Ratio c/b.
			SERIES A.		
1.	147.8	9.6	106.8	14.3	11.1
2.	156.1	13.8	117.7	7.6	8.5
3.	149.2	19.2	105.0	9.6	5.5
4.	152.0	19.6	90.0	26.9	4.6
5.	151.0	12.9	136.7	12.3	10.6
6.	152.9	16.9	100.1	19.7	5.9
			Average of Series A . . .		**7.7**
			SERIES B.		
1.	101.5	17.3	71.9	7.1	4.2
2.	100.9	21.6	lost	lost	—
3.	100.9	20.0	65.3	5.5	3.3
4.	100.7	12.8	73.5	11.2	5.7
5.	100.3	13.5	lost	4.7	—
6.	100.5	15.7	64.4	7.4	4.1
			Average of Series B . . .		**4.3**
			SERIES C.		
1.	49.7	13.3	28.3	3.6	2.1
2.	"	14.9	22.7	3.6	1.5
3.	"	11.7	27.4	6.3	2.3
4.	"	lost	24.9	2.9	—
5.	"	16.9	21.8	3.9	1.3
			Average of Series C . . .		**1.8**

SERIES D.

1.	9.4	7.8	1.8	1.4	0.2
2.	10.4	8.7	1.0	1.9	0.1
3.	9.5	4.9	2.2	4.7	0.4
4.	9.5	5.7	2.0	2.7	0.3
5.	9.6	8.7	1.4	3.2	0.2
6.	9.6	7.8	2.0	3.3	0.3
			Average of Series D . . .		0.3

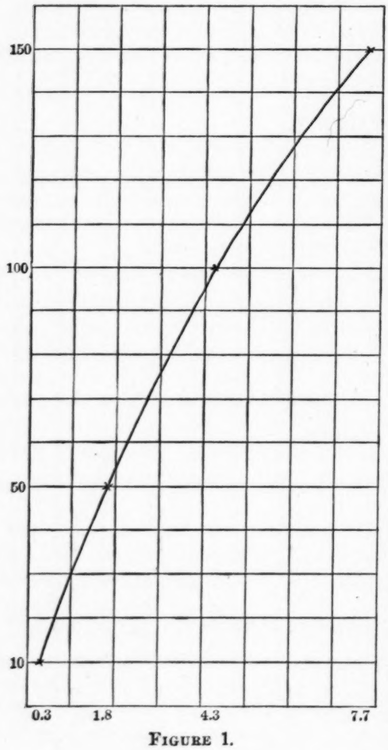

FIGURE 1.

A study of the above table will show that there is apparently a considerable amount of unreduced antimony in solution, and that all the antimony taken is not accounted for, except in Series D, in which it is less than the amount apparently found. Though the impurities in the zinc were probably too slight to influence the reaction in any way, yet the amount of zinc, which was purposely small in order to avoid the introduction of large quantities into the solutions to be titrated, was perhaps insufficient for reduction. It is not unfair to suppose that a more complete reduction would have given the same ratios between the precipitated antimony and that evolved as hydride. As to the inequality between the amounts of antimony taken and found, we think that this may be explained by the errors in the titration of such small amounts.

In spite of these criticisms of the above results, it seems to us that the study points to the conclusion that practically all of a small amount

of antimony, when introduced into the Marsh apparatus, can be converted to the hydride and collected as a metallic mirror. This conclusion is reached by a consideration of the averages, for each series, of the ratios of antimony precipitated on the zinc to that deposited in the heated tube. These ratios vary from 7.7 in Series A to 0.3 in Series D, and the rate of progression is not the result of chance. Plotting these results, we have the following curve (Figure 1), in which the ordinates are the amount of antimony taken and the abscissae the ratios of antimony precipitated on the zinc to that deposited in the heated tube.

From inspection of this curve, it seems to us reasonable to suppose that amounts of antimony under a milligram when introduced into the reduction flask would be practically converted to hydride, and we have proceeded on this assumption in the development of the method which follows, since in that method the amount of antimony usually taken for a determination in no case exceeds one tenth of a milligram and is usually considerably under that amount.

With the exception of an abstract of a paper by Rieckher,[6] we have found no previous study of the ratio of antimony deposited on the zinc to that evolved as hydride. In this abstract the ratio is said to be between 92 to 8 and 96 to 4, i. e., from 11.5 to 24, but the data for this conclusion are not given. As the original paper of Rieckher is not accessible to us, we can only assume that the concentration of the antimony ions must have been much greater than in our experiments.

II. The Temperature and Cross-Section of the Deposition Tube.

The preparation of pure, gaseous antimony hydride has been accomplished in recent years by Stock and Doht[7] and by Stock and Guttmann.[8] The pure gas has been shown by these authors to have in many respects quite different properties from those of the various mixtures of hydrogen and hydride of antimony which have been in the hands of so many investigators. As to the property which concerns us in this investigation, the decomposition of the hydride by heat, Stock and Guttmann have shown that the pure gas decomposes slowly at ordinary temperature, but very readily in the presence of catalytic agents, notably antimony itself. In the case, however, of the mixture of hydrogen and antimony hydride which comes from a Marsh apparatus containing minimal amounts of antimony, the concentration of

[6] Neues Jahrbuch. d. Pharm., **28**, 10 (1867 ?); ref., Jahresber. 1867, 255.
[7] Ber., **34**, 2339 (1901); **35**, 2270 (1902).
[8] Ibid., **37**, 885 and 901 (1904).

the hydrogen is very great compared with that of the hydride, and the decomposition would not take place except at a relatively high temperature.

We have, therefore, no data as to the decomposition point of antimony hydride in such dilution, since investigators of this point, for example Brunn,[9] have dealt with mixtures containing much greater amounts of antimony. Brunn gives the decomposition point of antimony hydride as 150°; of arsenic hydride as 230°; but the amount of each in the mixture is not stated. Furthermore, in our work the differences in the amounts of antimony are relatively so slight in comparison with the large amount of diluting hydrogen that the temperatures required for decomposition should not vary within wide limits. As the amount of antimony to be estimated in mirror form should not exceed 0.1 mg. of antimonious oxide, the question to be considered is the lowest temperature at which the hydride from this amount, mixed with a relatively very large volume of hydrogen, would be decomposed when passed through the heated tube. At the same time, with a view to the possibility of separating small amounts of arsenic and antimony by the difference in decomposition points of the diluted hydrides, we included in our investigation the decomposition point of diluted arsenic hydride. While it is well known that antimony hydride, in any dilution, decomposes at a lower temperature than arsenic hydride at equal dilution, there were no exact data to guide us.

At the beginning of the study, the tube was heated just behind the drawn-out portion, or, as we shall call it, the capillary. It was very soon found that even with small portions of antimony there was a tendency to deposition in the wide part of the tube back of the heated portion, since the larger surface offers greater chance for deposition of the rapidly condensing antimony. It was then found necessary to heat the capillary itself, which had the effect of concentrating the deposit at the desired place just in front of the heated space.

For determining the decomposition temperature, we used the thermoelectric method of Le Chatelier, employing for the purpose a couple of which the wires were platinum and an alloy of platinum with ten per cent of rhodium. The couple was standardized by determining the electromotive force (in micro-volts) produced by heating the junction in the vapor of boiling naphthaline (218°), diphenylamine (302°), and sulphur (445°). With these three boiling points as ordinates and the corresponding electromotive forces as abscissae, a perfectly straight line was obtained. As the temperature to be measured did not exceed 700° or fall below 200°, it was justifiable to extend this line and use

[9] Ibid., **22**, 3202 (1889).

it as a means of determining the temperatures by observation of the electromotive forces produced.

The study, as far as it concerned the separation of arsenic and antimony, is not completed, hence the results are reserved for another publication. Sufficient data were obtained to show that there was a possibility of separating arsenic and antimony by the difference in decomposition points of their diluted hydrides, and the investigation will be continued in this laboratory. Concerning the arsenic hydride, it will be sufficient to say that an amount of diluted hydride corresponding to 0.04 mg. of arsenious oxide is completely decomposed at 340° if the length of capillary heated is 3.5 cm.; at 410° if the length is 2 cm.; and at about 450° if the length is 1 cm. Conversely, no arsenic is deposited from this amount at 330° with a heating length of 1 cm.; none at about 300° if the length is 2 cm.; and none at about 250° if the length is 3.5 cm.

We were unable to get as definite results on the decomposition of antimony hydride, since the difficulty in deposition of the antimony mirror on the glass tubing used, which was afterwards solved as explained later, prevented the results from being uniform. We think, however, that we are safe in saying that amounts of hydride from 0.1 mg. antimonious oxide and under are entirely decomposed at a temperature of 300° and a heating length of 2 cm.

Having shown that practically all the antimony may be evolved as hydride from the small amounts to be used in our work, and that the hydride, diluted with hydrogen, can be entirely decomposed by heating the capillary through which the gases pass at a temperature which is easily controlled, we then proceeded to develop a method for estimating minimal amounts of antimony.

The Apparatus.

The apparatus [10] is essentially the same as that proposed by Sanger for the estimation of small amounts of arsenic. Slight modifications of this have been introduced by subsequent workers, many of whom have overlooked the original article. As shown in the figure, the parts comprise a constant hydrogen generator, two reduction flasks, and two heating tubes, so that duplicate determinations may be carried out at

[10] This apparatus, which is shown in Figure 2, is essentially the same as that described, but not illustrated, in the paper of Sanger (1891) above referred to. An apparatus of practically the same principle is shown on page 226 of Volume II of the Final Report of the Royal Commission on Arsenical Poisoning (Appendix 22, Report to the Commission by McGowan and Finlow on the methods employed in testing for arsenic); London, Eyre and Spottiswoode, 1903.

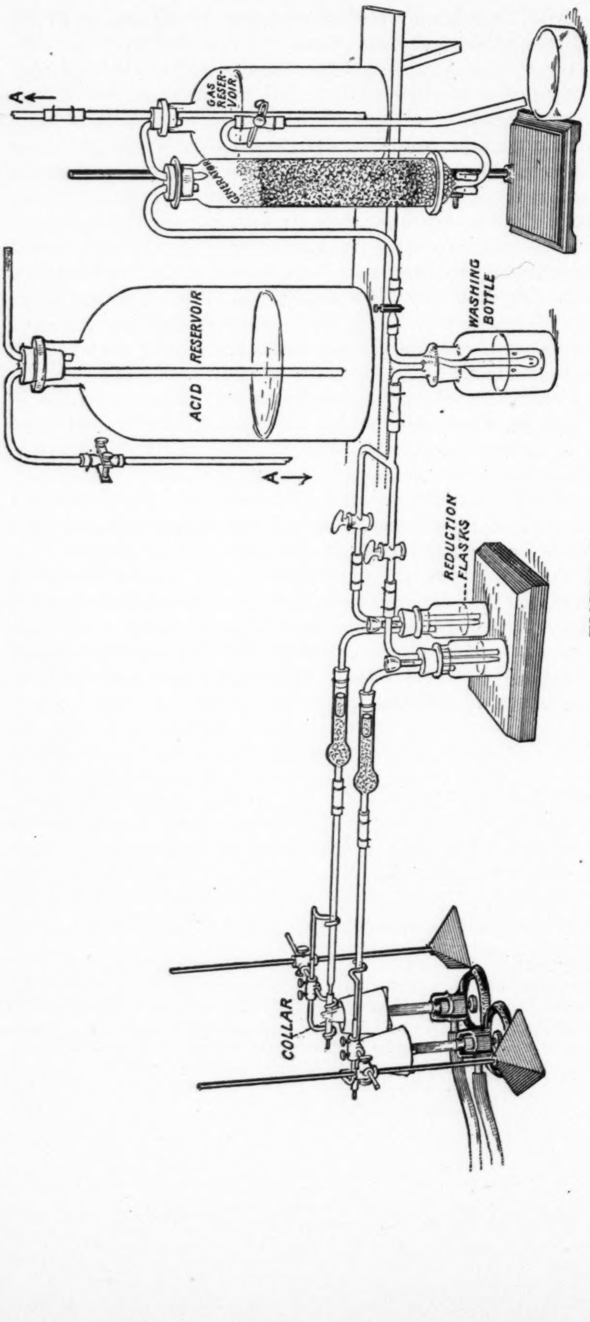

FIGURE 2.

Apparatus for the Determination of Small Amounts of Antimony.

the same time. The generator which we have found most convenient is one proposed by Richards, and is similar to the forms described by him some years ago.[11] Any form of constant generator will answer which provides for withdrawal of the spent acid without disconnection. The zinc in the generator is conveniently sensitized, according to the suggestion of Gooch,[12] by brief treatment with a solution of cupric sulphate and subsequent washing. The acid is sulphuric, at a dilution of one to eight. The hydrogen from our generator shows no arsenic or antimony when run for hours at a time.

As the hydrogen with which the antimony hydride is heated must contain no hydrogen sulphide, as hereafter shown, the hydrogen from the generator is passed through a ten per cent solution of cupric sulphate contained in an Allihn or other suitable washing bottle. From this, the hydrogen, which needs no further purification, passes to a Y-tube with two glass stopcocks. To these stopcocks are attached the reduction flasks, which are wide-mouth bottles of 60 to 75 c.c. capacity. These are fitted with a pure rubber stopper with three holes. Through one hole passes, to the bottom of the bottle, a right-angle tube connected with the stopcock; through the second a tube passing nearly to the bottom of the bottle and extending 3 to 5 cm. above the stopper. The upper end of this tube is open, the lower somewhat constricted. In the tube is placed a small funnel, blown from narrow tubing, through which the solution to be reduced is added. The third hole in the stopper carries the right-angle delivery tube for the hydrogen which passes just below the stopper. On its upper end is a rubber stopper over which is placed a 15 cm. (total length) tube filled with calcic chloride in fused sticks. We have found it convenient to half fill the tube with calcic chloride, and then to introduce a second, smaller tube filled with the chloride. By this arrangement the rear portion of the chloride, which soon becomes moist, may be frequently and conveniently renewed without disturbing the rest.

To the calcic chloride tube is connected the hard glass reduction tube drawn out to a straight capillary and ending in a capillary point. This tube is supported throughout its length by three adjustable brass hooks (No. 6 gauge, 4.1 mm.). The middle hook, which has a shank 10 cm. long, is fastened to a stand by the ordinary double clamp. On the top of the shank and about two thirds the distance from the clamped end are soldered two ordinary screw connectors at right angles to the shank. The other hooks, which are somewhat longer than the first, are bent at right angles in the plane of the table and their shanks

[11] Amer. Chem. Jour., **20**, 189 (1898).
[12] Amer. Jour. Sci., (3) **48**, 292 (1894).

pass in opposite directions through the connectors, in which they can be clamped by the screws. The end hooks are thus capable of being raised or lowered or of being moved laterally, so that the combination of the three hooks will support any tube and capillary.

We found it best to protect the capillary from direct contact with the flame, and at the same time to secure a more uniform heating by enclosing it in a brass tube or collar which is slipped over the capillary and rests on the two anterior hooks of the support. This collar is 5 cm. long, with an outer diameter of 6 mm. and an inner of 4 mm. It is heated towards the anterior end by the tip of a flame 5 to 6 mm. high from a burner with a good air supply and protected by a conical chimney. We assume that under these conditions the capillary is heated, through a space of 3 cm., at about 500°.

The Preparation of Standard Mirrors.

A standard solution of antimony was made by dissolving 2.3068 gr. of recrystallized tartar emetic in water and making up to one liter. This solution (I) contains 1 mg. of antimonious oxide in each cubic centimeter. Of solution I, 10 c.c. were diluted to a liter, giving a solution (II) containing 0.01 mg. per c.c. The tartrate offers the most convenient and accurate solution, and we satisfied ourselves that the presence of the tartrate ions had no effect whatever on the deposition of the mirror. The strength of solution I was also checked by analysis.

The zinc used in the reduction flask was the same as that used in the generator, but in smaller pieces, averaging perhaps 1 cm. in their longest dimension. The weight used was from three to five grams. This zinc, which is obtained of the New Jersey Zinc Company of New York, contains not over 0.019 per cent of lead and not more than 0.013 per cent of iron; hence the evolution of hydrogen by its contact with dilute sulphuric acid is slow. Platinum or other sensitizing agents, either in form of foil or as a deposit on the zinc, cannot be used, as we have proved by trial, since they show a tendency to hold back antimony even greater than in the case of arsenic.[13] We had recourse, therefore, to hydrochloric acid, in a dilution of one to ten, of which we use exactly 20 c.c. for each run. The hydrochloric acid, which is obtained of Messrs. Baker and Adamson, of Easton, Pa., contains no antimony, and only about 0.02 mg. of arsenious oxide per liter, an

[13] The discussion as to the effect of other metals on the evolution of arsenic hydride has been revived in recent years through the endeavors to increase the delicacy of the Marsh test for arsenic. This question, as applied to arsenic and antimony, will be taken up by one of us in a future paper.

amount which is inappreciable in our work on antimony.[14] By use of hydrochloric acid and purification of the hydrogen from the generator, there is no necessity for purification of the hydrogen from the reduction flask, provided sulphur compounds reducible to hydrogen sulphide are absent. Whenever the hydrogen contains hydrogen sulphide, the deposit in the heated tube is more or less reddish-yellow in color, due presumably to the presence of antimonious sulphide.

The fused sticks of calcic chloride used for drying (Merck) dissolved clear in water, and the solution showed an alkalinity of not over 0.3 per cent. We have seen no reason to believe that hydride of antimony is held back by this preparation, nor has there been any loss of antimony observed from an unduly moist condition of the chloride. We have, however, kept the chloride as active as possible by refilling the rear half of the tube with fresh chloride after every half dozen runs, as explained, or when the accumulation of moisture becomes noticeable. When not in use, the tubes are kept stoppered.

The selection of hard glass tubing is a matter of the highest importance for the success of the method. We used at first a German glass, source not known to us, which had been used in arsenic work without apparent disadvantage. This glass had a slight brown color after long ignition. Antimony mirrors deposited on this, under the conditions about to be described, were often white and not clearly defined. We next tried a sample of American glass, but this gave the brown color on ignition still more, and the deposits of antimony were entirely white. Next a Jena glass, which on ignition gave the well-known opaque appearance, and on which the mirrors were also entirely white. Finally we resorted to a glass of Kavalier, which did not give any color or opacity on long heating. The deposits of antimony on the capillaries drawn from this glass were satisfactory, and it was used in the preparation of the standard mirrors.[15]

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[14] This would mean not over 0.00004 mg. of arsenic in the amount of hydrochloric acid used, which is beyond the limit of the delicacy of the process as applied to arsenic.

[15] A cursory qualitative examination of the different samples of tubing showed no marked points of difference except that the fourth tubing contained no barium, while the others did. The amount of barium in the others was proportional to the degree of change in appearance of the mirror produced on the samples. Lack of time prevents an investigation on this point, and an opinion as to the influence of the barium, if any, would be mere conjecture; as, for example, whether the barium oxide could act catalytically in causing an oxidation of the antimony, since it seems probable that the white deposit is due to an oxide of antimony. In the absence of any definite knowledge on the matter one can only determine the availability of a sample of glass by actual trial.

The glass tubing varies from 5 or 6 mm., inside diameter, to 7 or 8 mm. outside. The inside of the tube should be thoroughly cleaned before use. For this purpose a bundle of tubes is entirely immersed for some time in concentrated sulphuric acid to which sodic chromate has been added. The tubes are then washed, dried, and stored away from dust. In drawing out the capillary, care should be taken to draw to the same outside diameter and as nearly as possible to the same length. If one starts with tubes of as nearly equal size as possible, and observes these conditions, a capillary of nearly constant bore is obtained. It is on this uniformity of bore that the gradation of the standards depends. One should therefore at least draw the tubes to the same diameter, since this condition is easily governed and is the chief factor in determining the bore. We have used for this purpose a Brown and Sharpe wire gauge, and have drawn the tubing to gauge No. 13, which corresponds to 1.8 mm., or 0.072 inch.

In beginning the run, three to five grams of zinc are placed in the reduction flask, which is then attached at one end to the stopcock of the constant generator, at the other to the drying tube. To the latter is then attached the ignition tube, with the collar over the capillary. 20 c.c. dilute hydrochloric acid are added through the funnel tube, and the apparatus may be tested for tightness by closing the end of the capillary with the finger while adding the acid. The hydrogen is then turned on from the generator, and, when the air is expelled, is lighted at the end of the capillary and turned down to a height of about one millimeter. It is important that this height be maintained as nearly as possible throughout the run and that the flame should burn steadily, since an irregular flow of hydrogen results in an uneven deposit of antimony. After the apparatus has been in action for five or ten minutes, the measured amount of antimony is added to the reduction flask through the funnel, which is then rinsed into the flask with a little water. No air is introduced into the apparatus if the funnel is sufficiently small compared to the tube in which it is set, and if the lower end of the tube is constricted.

The deposit of antimony makes its appearance in five to ten minutes, and is completely deposited in thirty, though we have usually waited forty to fifty minutes, to avoid the possibility of loss. We have satisfied ourselves that all the antimony is deposited from the hydride at this point, since a further heating along the tube gives no mirror.

The tubes containing the mirrors are sealed at each end and mounted in a frame, as shown in the plate. This frame is 185 mm. by 70 mm. outside, 135 by 35 mm. inside, and made of blackened wood 6 mm. in thickness. The tubes are fastened in holes passing

through the upper and lower sides of the frame. As the antimony mirrors are affected by moist air, and in the course of time by light, we take the precaution to seal the tubes and to keep the set of standards in the dark. The deterioration of the standards with time is not a serious objection to the method, since a fresh set can readily be made when desired.[16]

The amounts of antimony used by us in the set of standards shown in the plate are, in milligrams of antimonious oxide (Sb_2O_3) as follows: 0.005; 0.01; 0.015; 0.02; 0.025; 0.03; 0.035; 0.04; 0.045; 0.05; 0.06; 0.07. Above 0.07 mgr. it is of no advantage to make a mirror, as the recognition of the differences in the higher mirrors is difficult. These mirrors may be used as standards when viewed by reflected light, as shown in the upper set of the plate, but it is much better to use transmitted light. This is best arranged by mounting the frame in a box, similar in form to the fluoroscope, which may be of wood or metal. This box, about 25 cm. long and open at each end, is larger at the bottom than at the top, and carries a rabbet at the bottom through which the frame can be slipped. It is provided at the top with means of shading the eyes against all light except that which comes through the set of mirrors. If the box is held against a white surface, the mirrors gain greatly in sharpness, and smaller differences may be in this way detected when comparing mirrors obtained in an analysis. The lower part of the plate shows the set of standards when viewed by this device.

Analysis of Solutions containing Antimony.

To test the availability of the standard mirrors, a series of seven analyses was made of solutions in which the amounts of antimony were unknown to the analyst. The solutions were weighed to the second decimal place in a side-neck test tube of about 30 c.c. capacity. After the apparatus had been running for about ten minutes, a few drops of the solution were added to the reduction flask. If no mirror appeared within ten minutes, a larger portion of the solution was added, and if this again gave no mirror, the addition was continued. After the appearance of the mirror, the run was continued for thirty or forty minutes, until there was no probability of further deposit. By reweighing the test tube after the addition of the portion or portions which produced the mirror, the amount of solution taken was determined. The mirror obtained from this amount was then compared

[16] The suggestion of Panzer (Chem. Centralbl., **74** (1), 821 (1903), to seal standard arsenic mirrors with phosphorus pentoxide could probably be applied with advantage to the set of antimony mirrors.

with the standards and the amount of antimony read off. From the amount in the aliquot portion, the amount in solution was calculated.

Very often the mirror obtained from a given portion of the solution will be found too small or two large for estimation. In this case one can readily determine the proper amount of solution to be used.

The following table shows the results of these analyses :

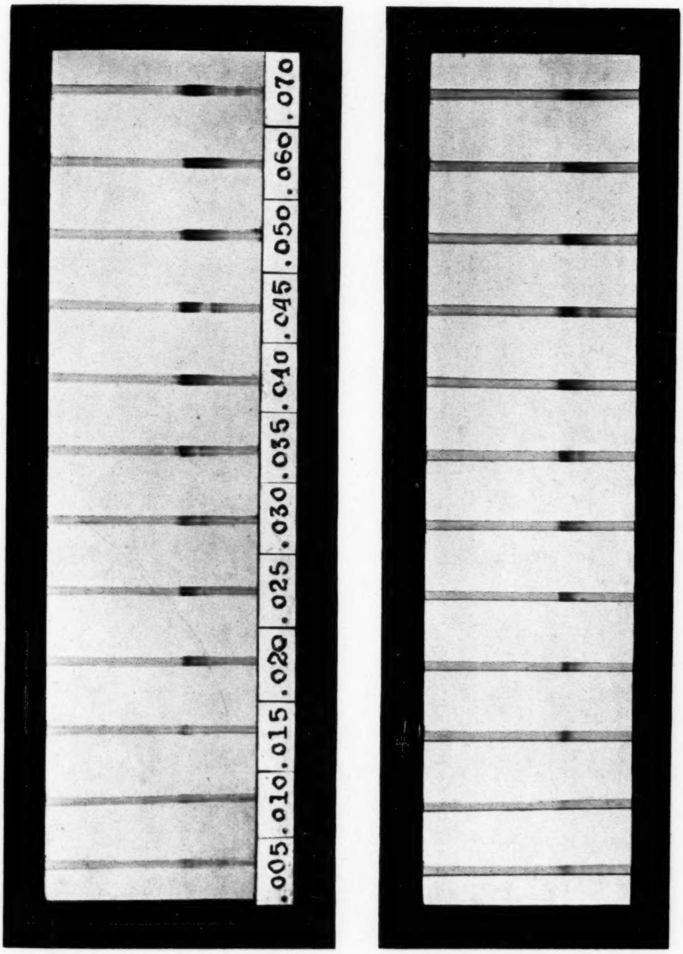
TABLE II.

No. of Analysis.	Standard Solution used.	C.c. of Solution taken.	Sb_2O_3 taken.	Total Weight Diluted Solution.	Weight Diluted Solution taken for Analysis.	Mirror Reading.	Sb_2O_3 found.	Sb_2O_3 found, Mean.	Per cent Sb_2O_3 found.
			mg.	gm.	gm.	mg.	mg.	mg.	
2	II	5	0.05	24.49	a) 5.56	0.014	0.06		
					b) 13.93	0.027	0.05	0.055	110
1	II	10	0.10	25.36	a) 11.64	0.038	0.08		
					b) 13.72	0.042	0.08	0.080	80
6	II	30	0.30	29.95	a) 3.14	0.035	0.33		
					b) 2.40	0.025	0.31	0.320	107
7	I	0.5	0.50	24.48	a) 1.91	0 043	0.55		
					b) 1.62	0.038	0.57	0.560	112
3	I	1.0	1.00	23.94	a) 0.83	0.038	1.10		
					b) 1.58	0.048	0.73	0.915	92
4	I	1.5	1.50	26.22	a) 0.72	0.040	1.46		
					b) 0.79	0.045	1.49	1.475	98
5	I	2.0	2.00	23.21	a) 0.45	0.038	1.96		
					b) 0 68	0.048	1.64	1.800	90
Average percentage									98

The results are as good as can be expected, considering the small amounts of antimony under estimation and the difficulty of reading the mirrors more accurately than within 0.002 or 0.003 mgr. The demand on the method made by these analyses is much more severe than would occur in actual practice. It is safe to say that the method will give a close approximation to the amount of antimony present in a given product, within the limits for which it is intended. It will serve also as a means of quickly, though roughly, estimating amounts which would require the ordinary analytical methods for an exact determination.

As to the delicacy of the process in the detection of minimal amounts of antimony, a mirror corresponding to 0.005 mg. can be detected and identified with certainty. With 0.001 mg. a faint deposit is seen. Yet the differentiation of amounts under 0.01 mg. presents some difficulty. Possibly the solution of the problem of how to sensitize the zinc properly in the Marsh process as applied to arsenic will enable one to detect smaller amounts of antimony with certainty. The question of the delicacy of the process has not so much concerned us, however, as its practicability. Its application to the determination of small amounts must of course be worked out for each particular problem. This does not come, however, within the scope of the present investigation, but certain applications of the method are under consideration in this laboratory.

HARVARD UNIVERSITY, CAMBRIDGE, MASS.,
January 1, 1907.



Standard Antimony Mirrors in Milligrams of Sb_2O_3.